

## A Multilayer Crystalline Surface Phase on a Melt of a Binary Alcohol Mixture

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Beamline(s): X22B

**Introduction:** The surface frozen layer's structure of binary mixtures of normal 1-alcohols ( $\text{CH}_3(\text{CH}_2)_n\text{OH}$ , denoted here  $\text{C}_n\text{OH}$ ) was investigated in a range of several degrees above the bulk freezing.

**Methods and Materials:** The >99% pure alcohols were obtained from Aldrich, and used as received. The x-ray measurements included specular reflectivity, grazing incidence diffraction and Bragg rod measurements, using the Harvard/BNL liquid surface reflectometer installed at beamline X22B.

**Results :** Unlike all alcohol melts studied to date (O. Gang et al., 1998), where a single crystalline bilayer forms at the free surface of the bulk liquid, we find a surface frozen layer consisting of four molecular layers in  $\text{C}_{18}\text{OH}(70\%)+\text{C}_{26}\text{OH}(30\%)$  mixture melt. As can be observed in Fig. 1 the X-ray reflectivity (XR) modulation period for this surface phase corresponds to a layer thickness of over 120 Å, while the thickness of a pure  $\text{C}_{26}\text{OH}$  bilayer was previously measured to be only 65.4 Å. A preliminary model fit of the measured XR, shown in Fig. 1 along with the corresponding surface-normal density profile (inset), confirms these conclusions. While the surface frozen bilayer, observed previously in normal-alcohols (M. Deutsch et al., 1995, O. Gang et al., 1998), was attributed to the tendency of alcohol molecules to form hydrogen bonds (HB) through their hydroxyl groups (the absence of which in normal alkanes leads to the formation of a surface-frozen monolayer, rather than bilayer (B. Ocko et al., 1997)), stacking of 2 bi-layers in a 4-layer system involves both HB and van der Waals interactions. Surface tension measurements of the same mixture, also show clearly the formation of the 4-layer by the twofold larger entropy gain upon surface freezing as compared to the simple bilayer case.

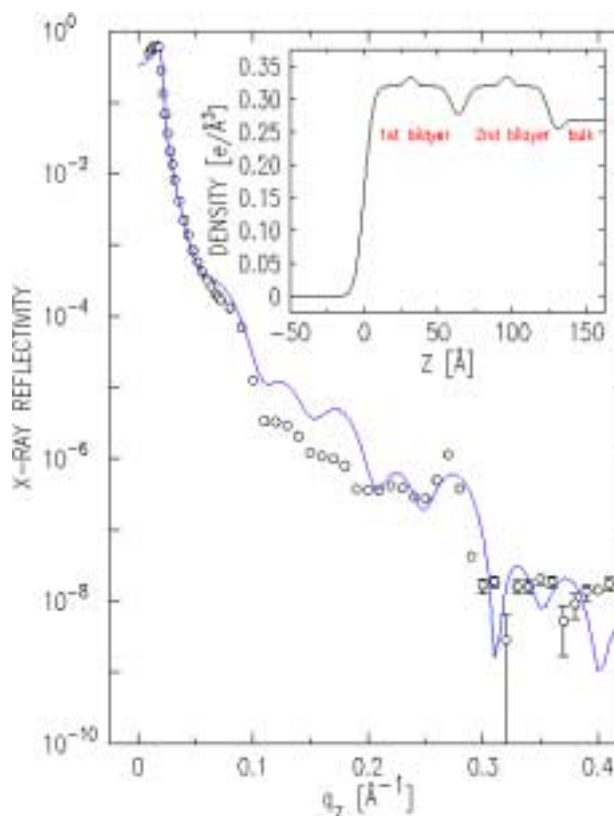
**Conclusions:** mixtures of alcohols of different length allow reaching corners of phase space not accessible using pure monocomponent melts. Thus, the study of binary, and perhaps ternary mixtures is likely to result in novel surface phases, such as the one obtained here. Further measurements are clearly indicated.

### References:

O. Gang et al., Phys. Rev. Lett. **80**, 1264 (1998); *ibid.* **82**, 588 (1999); Phys. Rev E **58**, 6068 (1998).

M. Deutsch et al., Europhys. Lett. **30**, 283 (1995).

B. Ocko et al., Phys. Rev. E **55**, 3164 (1997).



**Figure 1.** A preliminary model fit of the measured XR. The corresponding surface-normal density profile is shown in the inset.